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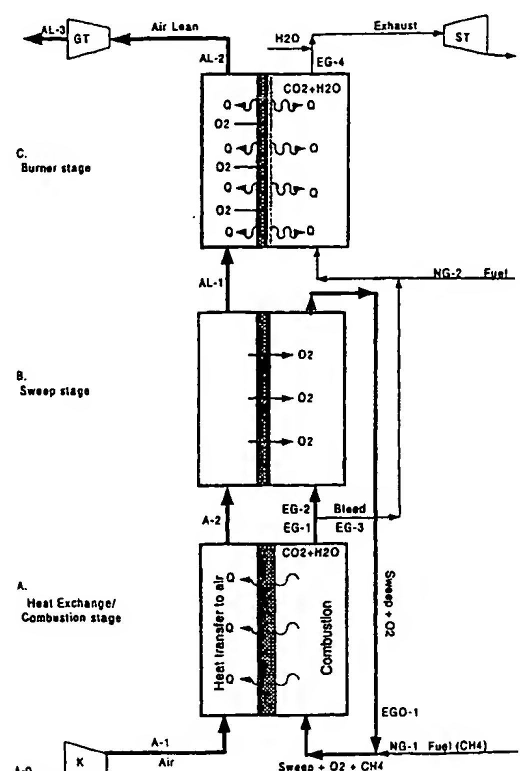
(54) Title: PROCESS FOR GENERATION OF HEAT AND POWER AND USE THEREOF



(57) Abstract: The present invention relates to an energy efficient process for generation of heat and power, where a carbon containing fuel is combusted with an oxidant in a MCM-burner for generation of heat, an oxygen depleted air stream and an exhaust gas with a high concentration of CO_2 and a low concentration of NO_x, where the oxidant is obtained by the following steps: a) a compressed air stream is preheated in a first stage (A) to a temperature level above 600 °C, b) the compressed and preheated air stream from stage (A) is fed to a second stage (B), including a mixed conducting membrane which is able to separate oxygen from the hot air stream fed to the retentate side of said membrane, where a hot sweep gas picks up the oxygen from the permeate side of said membrane and transports the oxygen to the first stage (A), where a carbon containing fuel is combusted with the oxygen enriched sweep gas for generation of heat utilised for indirectly preheating the air stream in stage (A) by means of a heat exchanger, c) passing the oxygen depleted air stream from said second stage (B) into a third stage (C) including the MCM-burner, where the depleted air stream flows on the retentate side of the MCM-burner membrane giving off oxygen to the combustion zone on the permeate side of the membrane , where oxygen (i.e. the oxidant) reacts directly with added fuel on the membrane or close to the membrane surface for generation of heat and a hot exhaust gas stream with a high concentration of CO_2 and low concentration of NO_x. The invention further relates to use of the generated heat, the generated hot depleted air stream and the generated hot exhaust gas stream from said process.

WO 01/79754 A1

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"Process for generation of heat and power and use thereof"

The present invention relates to an energy efficient process for generation of heat and power from a combustion process and use thereof.

Conventional combustion processes, used for carbon containing fuels, will in addition to producing the main end products carbon dioxide and water (steam), generate a considerable amount of heat (heat of combustion). A conventional combustion reaction between e.g. methane and oxygen will generate approximately 804 KJ per mol methane:

$$CH_4 + 2O_2 \dashrightarrow CO_2 + 2H_2O$$

When this combustion process is integrated with e.g. a power generating plant (i.e. gas turbines) or a chemical plant performing endothermic reactions, it is crucial that the heat of combustion is produced at low expenses and that the total energy loss from the combustion process is as low as possible.

Furthermore, due to the environmental aspects of CO_2 it is crucial that the emission of this component to the atmosphere is considerably reduced compared to the conventional processes. Conventional combustion processes produce an exhaust gas with a CO_2-concentration between 3 and 15% dependent on the fuel and the applied combustion- and heat recovery process. The reason the concentration is this low is because air comprises about 78% by volume of nitrogen. In high-temperature combustion processes in air, nitrogen will react with oxygen and produce the environmental hazardous gas pollutant NO_x.

A reduction in the emission of carbon dioxide to the atmosphere makes it necessary to either separate the carbon dioxide from the exhaust gas, or raise the concentration in the exhaust gas to levels suitable for use in different chemical processes or for injection in e.g. a geological formation for long term deposition or for enhanced recovery of oil from an oil reservoir.

CO_2 can be removed from cooled exhaust gas, normally discharged off at near atmospheric pressure, by means of several separation processes, e.g. chemical active separation processes, physical absorption processes, adsorption by molecular sieves, membrane separation and cryogenic techniques. Chemical absorption, for instance by means of alkanole amines, is considered as the most practical and economical method to separate CO_2 from exhaust gas. These separation processes, however, require a heavy and voluminous equipment and will consume a substantial amount of heat produced in the combustion process. Applied in connection with a power generating process, these separation processes will reduce the power output with 10% or more.

An increasement of the concentration of CO_2 in the exhaust gas to levels suitable for use in different chemical processes or for injection in e.g. a geological formation for long term deposition or for enhanced recovery of oil from an oil reservoir is possible by burning the carbon containing fuel with pure oxygen instead of air.

Commercial air separation methods (e.g. cryogenic separation or pressure swing absorption (PSA)) applied for producing pure oxygen require 250 to 300 KWh/ton oxygen produced. If these methods are used for supplying oxygen to a combustion process in a gas turbine cycle, these methods will reduce the net power output from the gas turbine cycle by at least 20%. The expenses of producing oxygen in a cryogenic unit will increase the price of electric power substantially and may amount to as much as 50% of the cost of the electric power.

However, a less energy demanding method than these separation methods is known from the European Patent Application 0658367-A2. The patent application describes an application of a mixed conducting membrane (MCM) integrated with a gas turbine system and where the membrane separates oxygen from a heated air stream.

To further improve the efficiency of this membrane method, a sweep gas is applied to reduce the partial pressure of oxygen on the permeate side of the membrane and thereby increase the flux of oxygen through the membrane; as e.g. described in US 5,562,754 and NO-A-972632.

To obtain a sufficient high flux of oxygen through the membrane a rather high temperature is required (>600°C). On the air side of the membrane this may be accomplished by combusting a fuel in the air stream, in a burner, to increase the temperature of the air fed to the membrane, for instance as disclosed in EP-A-0658367 and NO-A-972632. The most convenient and a less expensive method is to combust a carbon containing fuel in the air stream, e.g. a fossil fuel.

However, by means of this method the heated air stream will contain CO_2 generated in the burner. The concentration of CO_2 in the oxygen depleted air stream discharged from the retentate side of the membrane will be less than about 10% and in most cases as low as 3%. If recovery of all generated CO_2 in a combustion process is desirable, due to the environmental aspects of CO_2, an oxygen depleted air stream containing a low concentration of CO_2 is not desirable.

To obtain practical applications of mixed conducting membranes (MCM) when applied as an oxygen supplier in a combustion process the following criteria are essential:

1. The driving force of the oxygen transport through the membrane, the ratio between the oxygen partial pressure at the retentate (I) and the permeate (II) side of the membrane: log (pO_2 (I)/pO_2 (II)), has to be kept at a high level.

2. The membrane has to operate at high temperature levels (>600°C) to achieve a sufficient oxygen flux through the membrane. Thus air or any other gases in contact with the membrane must have high temperature.

To ensure that the driving force through the membrane is kept at a high level (criterion 1) oxygen on the permeate side of the membrane may be:

i) transported away from the membrane surface, by applying a sweep gas, or
ii) consumed by a chemical reaction (e.g. a combustion process) directly on the permeate side.

The method applying a sweep gas (i) is here named the MCM-sweep concept as illustrated in Sketch I and the method applying combustion (ii) is here named the MCM-burner concept as illustrated in Sketch II. The different streams in the figures are defined in Table 1.

The MCM-membrane material used in the MCM-sweep concept is here named the sweep material, and the MCM-membrane material used in the MCM-burner concept is here named the burner material. The burner material must be able to withstand much lower oxygen partial pressure than the sweep material.

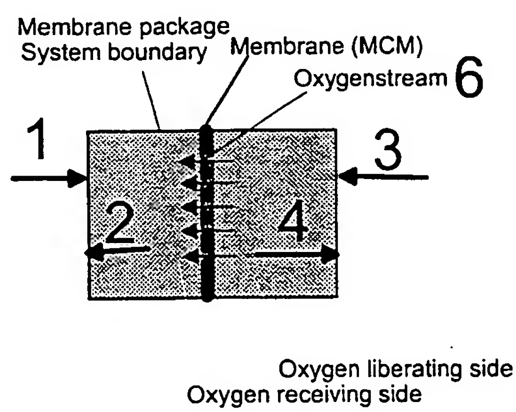
The mixed conducting membrane (MCM) is defined as a membrane made of materials with both ionic and electronic conductivity. The membrane is able to selectively transporting oxygen from the retentate (air) side to the permeate side of the membrane, resulting in a higher partial pressure of oxygen on the retentate side.

Table 1

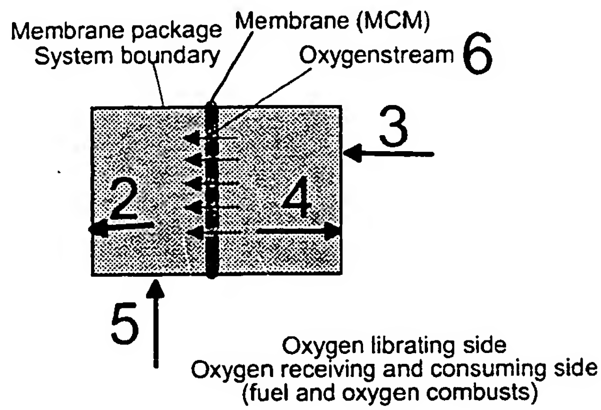
Stream No.	MCM-Sweep concept	MCM-Burner concept
1	(EG-xx) Exhaust gas, almost O2 free	Not part of burner concept
2	(EGO-xx) Exhaust gas, O2 enriched	(EG-xx) Exhaust gas, almost O_2 free
3	(AN-xx) Air Normal	(AN-xx) Air Normal
4	(AL-xx)Air Lean, O2 depleted	(AL-xx) Air Lean, O_2 depleted
5	Not part of sweep concept	(GS-xx) Gas (fuel) mixed with steam/CO_2
6	(OX-xx) Internal Oxygen transfer stream	(OX-xx) Internal Oxygen transfer stream

(The notation in Table 1 is used in the example as well. The two or three letter is referring to the specific stream in Sketches 1 and 2, e.g. NG = Natural Gas, and the notation xx after the letters is referring to any specific number used for that stream. These notations and definitions are used for detail description of the present invention.)

Sketch I Process streams, system boundary membrane package, the MCM-sweep concept:



Sketch II Process streams, system boundary membrane package, the MCM-burner concept:



The MCM-burner concept, as described in NO-A-972631, implies that a chemical reaction or a combustion reaction takes place directly on or close to the membrane surface.

The name MCM-burner refers to the combustion or burning (of fuel) taking place on or close to the membrane, but any other exothermic reactions consuming oxygen are here by definition included. A characteristic is that all heat is generated inside the membrane package.

However, to obtain an efficient transport of oxygen along the entire membrane in the MCM-burner and thus obtain an energy efficient combustion process, the air entering the membrane section has to be hot (>600 °C). Thus air has to be heated before entering the membrane (e.g. air compressed to 20 bar reaches only a temperature of 450°C). Air entering the membrane can be heated by heat exchange with hot outgoing air as described in NO-A-972631 and shown in Fig. 1 in the present invention. This results in pressure fall and cooling of the hot out-

going air before it enters e.g. a power generating turbine and implies a reduced power output from the turbine. Further heating of the membrane (and air) is done by the combustion reaction taking place directly on or close to the membrane surface consuming the oxygen, thus keeping a low oxygen partial pressure on the permeate side. Thus all heat is generated inside the membrane package in the MCM-burner.

In the MCM-sweep concept a transport gas is swept (i.e. sweep gas) over the membrane surface on the permeate side. The sweep gas may be H_2O and/or CO_2 and thus exhaust gas from a combustion process can be used as a sweep gas (as described in NO-A-972630). The sweep gas transports oxygen away from the membrane surface (maintaining low oxygen partial pressure on the permeate side), and fuel is added for combustion outside the membrane package. Thus, in a sweep concept only all heat is generated at the combustion place outside the membrane package creating the same problem as for the burner: The heat is generated at one place, but is needed two places. That is a) for preheating the air stream fed to the membrane and b) further heating the depleted air stream before entering e.g. a power generating turbine or for supplying heat to endothermic reactions.

Both concept i) and concept ii) ensure that a low partial pressure of oxygen on the permeate side is maintained. If not, the transport of oxygen from the retentate to the permeate side will be reduced and in some time stop, due to declining difference in the oxygen partial pressure.

The second criterion (2) regarding heating gases entering the membrane implies that heat exchange is an important part of the total process. Thus, in all the different applications utilising mixed conducting membranes the air stream entering the membrane has to be heated. Normally this is obtained by heat exchanging the "cold" air stream entering the membrane with the hot oxygen depleted air stream leaving the membrane. A carbon containing fuel could also be injected to combust part of the oxygen in the air stream entering the membrane,

and thus heat the air directly. However, as mentioned earlier, this method will generate an oxygen depleted air stream containing CO_2.

A sufficient high oxygen flux (for practical use) through the membrane will first arise at temperatures above 800°C and will further increase with increased temperature. Thus, to have a high oxygen flux through the membrane, air has to be preheated before entering the membrane.

The main object of the present invention was to arrive at an energy efficient process for generation of heat and power.

Another object of the present invention was to arrive at a process where a carbon containing fuel is combusted with an oxidant in a MCM-burner for generation of heat suitable for direct use in different processes and an exhaust gas with a high concentration of CO_2 and a low concentration of NOx suitable for direct use in different processes or for injection in a geological formation or for other forms of deposition

Furthermore, another object of the present invention was to arrive at an energy effective method for preheating an air stream fed to a MCM-burner without generating CO_2 in the air stream and without lowering the temperature of the air stream leaving the MCM-burner.

The inventors found that the described objects are fulfilled if the MCM-burner concept is combined with the MCM-sweep concept. Thus, the process according to the present invention will comprise three stages; i.e. a heat exchange/combustion stage, a sweep stage and a burner stage.

The scope of the invention in its widest sense is an energy efficient process for generation of heat and power where a carbon containing fuel is combusted with an oxidant in a MCM-burner for generation of heat, an oxygen depleted air stream

and an exhaust gas with a high concentration of CO_2 and a low concentration of NOx, where the oxidant is obtained by the following steps:

a) a compressed air stream is preheated in a first stage A to a temperature level above 600°C,

b) the compressed and preheated air stream from stage A is fed to a second stage B, including a mixed conducting membrane which is able to separate oxygen from the hot air stream fed to the retentate side of said membrane, where a hot sweep gas picks up the oxygen from the permeate side of said membrane and transports the oxygen to the first stage A where a carbon containing fuel is combusted with the oxygen enriched sweep gas for generation of heat utilised for indirectly preheating the air stream in stage A by means of a heat exchanger,

c) passing the oxygen depleted air stream from said second stage B into a third stage C including the MCM-burner where the depleted air stream flows on the retentate side of the MCM-burner membrane giving off oxygen to the combustion zone on the permeate side of the membrane where oxygen (i.e. the oxidant) reacts directly with added fuel on the membrane or close to the membrane surface for generation of heat and a hot exhaust gas stream with a high concentration of CO_2 and low concentration of NO_x.

By using recirculated sweep gas, heat is transferred from the combined heat exchange/combustion stage to the sweep stage. In the heat exchange/combustion stage, air is heated to a temperature suitable for the sweep stage (i.e. for the MCM-sweep membrane to transport oxygen). Thus by combining the heat exchange/combustion stage and the sweep stage it is possible to both heat the air stream and generate oxygen to the combustion stage. A combination of these two stages with a burner stage will further a) improve the total energy efficiency in the

process and b) heat the air stream fed to a burner membrane without generation of CO_2. Thus, this combination of the different stages takes advantage of the fact that a higher driving force for the oxygen transport through a burner membrane can be obtained due to the direct consumption of oxygen (i.e. direct combustion) and thus the hot oxygen depleted air stream from a sweep membrane can be fed to a burner membrane.

The oxidant used in the first stage is the oxygen enriched sweep gas from the second stage, and the applied sweep gas is the combustion product (exhaust gas) from the first stage.

The generated heated oxygen depleted air stream in the MCM-burner stage can be utilised to generate power by depressurizing the oxygen depleted air stream in a turbine and further recovery of the heat by steam generation and further use of the steam in another power generating turbine.

The generated exhaust gas from the MCM-burner stage can be utilised to generate power by depressurizing the hot exhaust gas in a turbine and further recovery of the heat by steam generation and further use of the steam in another power generating turbine process.

Generated exhaust gas, after separation of the water in the exhaust gas, may be utilised for injection in a geological formation for long term deposition or for enhanced recovery of oil from an oil reservoir and other forms of deposition.

Furthermore, the generated exhaust gas can be used in production of e.g. syngas (CO and H_2).

Furthermore, produced heat from the process according to the present invention may be utilised in endothermic reactions as e.g. in syngas (CO and H_2) production.

The invention will be further explained and envisaged in the example and the figures.

Fig. 1 shows a flow sheet for the process according to the present invention.

Fig. 2 shows a more detailed flow sheet for the process according to the present invention.

Fig. 3 shows a burner process without an integration with a MCM-sweep stage.

Fig. 1 shows the main stages and the corresponding streams in the process according to the present invention. The process comprises three main stages where the ordering of the stages is as follows: a heat exchange/combustion stage A, a MCM-sweep stage B and a MCM-burner stage C.

The combustion/heat exchange stage A may be arranged in one combined stage or divided in two separate stages. Thus all such individual solutions are included in stage A in the present invention.

In Fig. 1 the air and the sweep/exhaust gas streams are shown in cocurrent flow direction. But any direction of streams are valid (i.e. countercurrent or cross flow) for the combined principle as long as the ordering of the stages is (in direction of incoming air) as follows: a heat exchange/combustion stage, sweep membrane stage, burner stage.

In the Figs. 1-3 the streams are numbered according to Table 1. The air stream A-0 is compressed in a compressor K to increase the partial pressure of oxygen. The compressed air stream A-1 is then preheated in stage A. Stage A includes a combustion step where a carbon containing fuel NG-1 is combusted and the

generated heat is indirectly heating the air stream A-1 by means of a heat exchanger. When the air has reached a temperature level sufficient to obtain significant fluxes through the membrane, the hot air stream A-2 enters the sweep stage B. In the sweep stage, including a mixed conducting membrane, the membrane separates oxygen from the air stream A-2. The oxygen lean air stream AL-1 leaving the sweep stage is then entering the burner stage C, including a mixed conducting membrane, where more oxygen is separated, from the oxygen lean air stream AL-1, through the MCM-burner membrane. The oxygen is transported to the combustion zone on the permeate side of the burner membrane, and reacts with added fuel NG-2. Thus a combustion is taking place on or close to the burner membrane surface, and will indirectly increase the temperature in the oxygen depleted air stream. Thus the leaving oxygen depleted air stream AL-2 will have a higher temperature than the entering air stream AL-1. Furthermore, a hot exhaust gas stream EG-4 will leave the MCM-burner.

The generated hot exhaust gas from stage A, EG-1, containing mainly CO_2 and steam, is almost oxygen free, and is fed to the sweep stage B, stream EG-2, where it is applied as sweep gas to pick up oxygen on the permeate side of the membrane in stage B. The oxygen enriched sweep gas stream, EGO-1, is fed to the heat exchange stage A where it is applied as an oxidant in the combustion reaction.

The maximum temperature difference between the air stream A-2 and the sweep gas stream EG-1 is possible to control. This is important because of limitations in maximum temperature difference across the membrane material, due to thermal stress, which can cause cracks in the material.

From the almost oxygen free sweep gas stream EG-1 leaving stage A, a bleed is taken out (EG-3) and fed to the burner stage. A bleed stream (EG-3) is taken out to balance mass due to oxygen transport through the membrane in stage B and fuel addition NG-1. The bleed EG-3 is taken out from the sweep/exhaust gas

stream EG-1 at this position in the membrane module to have minimum loss of fuel and oxygen. The generated heated bleed stream may be applied for a power generating plant or as a fuel transport gas for the burner stage.

Fuel NG-2 is added to the bleed gas EG-3 entering the permeate side of the MCM-burner membrane. Then a combustion of fuel takes place with oxygen transported through the MCM-burner membrane. Both the air stream AL-2 and the exhaust gas stream EG-4 have by means of combustion been heated inside the burner stage. In the figures these streams are shown entering turbines for power generation. However, other applications are possible to utilise the heat and the pressure of the streams, e.g. endothermic reactions like steam reforming for production of syngas.

For more specific and detailed description of the present invention Fig. 2 is used. Numbers underscored are put on the figure to help explaining the functionality. Snake arrows are symbolising heat flux and small straight arrows symbolise oxygen flux through the membranes.

A main flow of compressed air A-1, compressed in compressor K, is entering stage A. The main inlet flow is sent to a large surface area in all stages A, B and C. In stage A a heat exchange wall 16 is applied to achieve a high heat transfer rate from the combustion side 11 to the air side 10. This wall can be made of any material which is able to transfer heat and withstand the high temperatures and other conditions present on the two sides 10 and 11. Evidently selection of materials is also dependent upon individual designed solutions, especially whether combustion is taking place in a separate combustion chamber prior to the heat exchanger or if a combined combustion/heat exchange solution is used.

In stage B the large surface area consists of the oxygen transporting membrane 18. The large membrane surface area is needed to have a high total oxygen transporting rate from the retentate 12 to the permeate side 13. Also in stage C, in

the burner stage, a large surface area is needed. Here the large surface area is needed both for the high rate of heat and for the oxygen transfer through the membrane 20. Thus oxygen is transported from the retentate or the oxygen depleted air side 14 to the permeate side of the membrane 15, where oxygen reacts in the combustion zone 21 with added fuel NG-2. Thus this combustion reaction generates heat that partly is transported in the opposite direction of the oxygen, from the permeate 15 to the retentate side 14, to heat the air stream and partly rise the exhaust gas temperature. Thus, both the lean air AL-2 and the exhaust gas EG-4 reach a maximum temperature when leaving the burner stage.

In stage B, the sweep stage, the membrane is separating the sweep gas side 13 and the air side 12 in a gas tight manner. Thus sealing is an important part of the design. The membrane wall shown in Fig. 2 consists of a support layer 17 giving strength and the very thin oxygen selective transporting membrane layer 18.

In the burner section C the membrane may comprise the same layers, but be made of preferably a different material composition due to different conditions. In Fig. 2 this is shown by the support layer 19 and the thin membrane layer 20. Also a third layer 21 is shown, a catalyst layer. A catalyst layer may not be necessary, but is here shown to represent that a combustion reaction is taking part on or close to the membrane surface, here called the combustion zone.

For the functionality of the process a pressure increasing device (not shown in the figures) has to be included for the hot circulating sweep gas (to overcome the pressure fall). This pressure increasing device has to operate at very high temperatures, and therefore probably an ejector (venturi) is the best choice. Dependant upon the pressure fall and the flow rate in the circulating sweep gas loop, a specific amount of high pressure gas has to be used to give the driving force for the ejector. The driving gas could be high pressure steam or CO_2. Several ejectors could be used either in parallel or in series, or in a combination.

Furthermore, the process has to be regulated in such a way that the amount of oxygen separated from air (through the sweep and the burner membrane) is balanced to the amount of fuel added according to the stoichiometry of the combustion reaction.

In Figs. 1 and 2 only one option with respect to the flow arrangements for the combined burner/sweep concept is shown (cocurrent flow), but also cross flow or countercurrent flow or combinations of these are possible between the three main sections; A, B and C (the heat exchange/combustion stage, the sweep stage and the burner stage). The individual arrangement between the three main stages should always be (in direction of incoming air): first the heat exchange /combustion stage, second the sweep stage and third the burner stage (involving combustion and heat exchange).

The order of the main stages is ensuring that the air stream fed to the sweep stage both is preheated and oxygen rich (level present in air). This order is a characteristic of the present invention.

There is also a possibility (flexibility) to exchange or transfer heat to air in the sweep stage B. The amount of heat exchanged in this stage is dependent upon maximum allowable temperature difference across the membrane wall, and is controlled by the circulating sweep gas. Thus the two stages A and C generate heat and the three stages A, B and C are able to transfer heat to the air streams. Thus the present invention gives a degree of freedom for adjusting the temperature levels in each of the three stages. This is illustrated in the example. Temperatures and amount of heat transferred in each stage are also inevitable dependent upon individual design of the membrane module system.

Example:

This example illustrates the capabilities and flexibility of the present invention. The example is based on a combined MCM-sweep and burner membrane process as presented in Figs. 1 and 2 and described above. In the process referred to in Table 2 air is preheated to 850°C and in Table 3 air is preheated to 1000°C. The streams for the whole process are presented in Tables 2 and 3. The notation of stream numbering in Tables 2 and 3 is the same as presented in Table 1 and also used in Sketches 1 and 2. Tables 2 and 3 show the flexibility of the present invention for heating air and sweep gas entering the sweep gas stage B, to different temperature levels, and at the same time keeping high and almost unchanged temperatures for the streams AL-2 and EG-4 leaving the burner stage (to e.g. a turbine). The mass flow of air, fuel, oxygen and the total heat generated is the same in the two Tables 2 and 3. The streams OX-1 and OX-2 are representing the oxygen flux through the sweep membrane and the burner membrane.

Table 2: Air preheat temperature 850°C

Stream no	A-0	A-1	A-2	AL-1	AL-2	EG-1	EG-2	EG-3	EG-4	EGO-1	NG-1	NG-2	OX-1	OX-2
Mole Frac														
CH4	0	0	0	0	0	0.00436	0.00436	0.00436	0	0.00422	0.83148	0.83148	0	0
C2+	0	0	0	0	0	0	0	0	0	0	0.12681	0.12681	0	0
CO2	0.00033	0.00033	0.00033	0.00034	0.00035	0.35867	0.35867	0.35867	0.35985	0.34652	0.03030	0.03030	0	0
N2	0.77738	0.77738	0.77738	0.80501	0.82892	0.00325	0.00325	0.00325	0.00322	0.00314	0.01080	0.01080	0	0
O2	0.20854	0.20854	0.20854	0.18041	0.15607	0	0	0	0.00004	0.03388	0	0	1	1
A	0.00933	0.00933	0.00933	0.00966	0.00995	0	0	0	0	0	0	0	0	0
H2O	0.00442	0.00442	0.00442	0.00458	0.00471	0.63371	0.63371	0.63371	0.63684	0.61224	0.00060	0.00060	0	0
Total Flow kmol/s	2.732	2.732	2.732	2.638	2.562	2.814	2.673	0.141	0.254	2.767	0.042	0.033	0.094	0.076
Total Flow kg/s	79.00	79.00	79.00	76.00	73.57	77.00	73.15	3.85	6.96	76.15	0.85	0.67	3.00	2.44
Temperature C	15.0	453.0	850.0	876.8	1169.5	906.0	906.0	906.0	1180.0	907.1	34.3	34.3	876.8	1169.5
Pressure bar	1.0	20.0	20.0	20.0	20.0	20.1	20.1	20.1	20.0	20.5	36.0	36.0	20.8	20.0
Enthalpy kW	-4091.8	31940.8	67378	67208.9	90200.7	-725000	-688750	-36250	-62159	-685870	-3700.7	-2917.1	2628.97	2914.99

Table 3: Air preheat temperature 1000°C

Stream no	A-0	A-1	A-2	AL-1	AL-2	EG-1	EG-2	EG-3	EG-4	EGO-1	NG-1	NG-2	OX-1	OX-2
Mole Frac														
CH4	0	0	0	0	0	0	0	0	0	0	0.83148	0.83148	0	0
C2+	0	0	0	0	0	0	0	0	0	0	0.12681	0.12681	0	0
CO2	0.00033	0.00033	0.00033	0.00035	0.00035	0.35938	0.35938	0.35938	0.35985	0.33449	0.03030	0.03030	0	0
N2	0.77738	0.77738	0.77738	0.81760	0.82892	0.00322	0.00322	0.00322	0.00322	0.00299	0.01080	0.01080	0	0
O2	0.20854	0.20854	0.20854	0.16760	0.15607	0.00142	0.00142	0.00142	0.00002	0.07058	0	0	1	1
A	0.00933	0.00933	0.00933	0.00981	0.00995	0	0	0	0	0	0	0	0	0
H2O	0.00442	0.00442	0.00442	0.00465	0.00471	0.63598	0.63598	0.63598	0.63684	0.59194	0.00060	0.00060	0	0
Total Flow kmol/s	2.732	2.732	2.732	2.598	2.562	2.007	1.806	0.201	0.254	1.940	0.060	0.016	0.134	0.035
Total Flow kg/s	79	79	79	74.7	73.57	55.00	49.50	5.50	6.96	53.80	1.20	0.32	4.30	1.14
Temperature C	15	453	1000	1026.3	1163.3	1063.6	1063.6	1063.6	1175.0	1058.6	34.3	34.3	1026.3	1163.3
Pressure bar	1.0	20.0	20.0	20.0	20.0	20.1	20.1	20.1	20.0	20.5	36.0	36.0	20.8	20.0
Enthalpy kW	-4091.8	31940.8	81142.5	79084	89661.6	-502540	-452290	-50254	-62225	-448120	-5224.6	-1393.2	4472.76	1350.92

Another characteristic of the present invention, shown in Tables 2 and 3, is that the temperature difference between air stream A-2 and the sweep/exhaust gas stream EG-2 (to stage B) can be kept at almost the same low level. This is important for limiting temperature stress to the membrane material.

As can be seen from Tables 2 and 3, it is possible to keep the temperature difference between the sweep and the air flow entering the sweep membrane stage at the same low levels. When air is preheated to only 850°C one would expect a much higher temperature difference between the hot sweep gas and the air compared to when air is heated to 1000°C. In the example, when heating air to 1000°C, a sweep gas temperature of 1063°C is obtained (EG-2, Table 2). This is almost the same difference as when heating air to only 850°C where the sweep gas temperature is 906° C (EG-2, Table 1). The temperature difference can be kept at the same low level by adjusting the mass flow of the circulating sweep gas. In this example the mass flow of sweep gas is increased from 53.8 to 76.15 kg/s to maintain the temperature difference when the temperature is decreased from 1000°C to 850°C. Thus, this shows the flexibility of the present invention to keep a low temperature difference between air and sweep gas.

Table 4 is representing a process where no sweep gas stage is integrated with a heat exchange stage. Thus, the incoming air to the burner membrane has to be heated as show in Fig. 3 by heat exchange with hot outgoing air. The air flow and the temperature of the leaving air stream AL-1 from the membrane burner are almost the same as shown in Tables 2 and 3 (ca. 1160°C), but after heat exchange with incoming air are lowered to about 760°C (AL-2) before leaving the burner. When taken into account that the membrane and the sealing materials have a maximum temperature limit of 12-1300°C (i.e. close to modern efficient gas turbines inlet temperatures), it further emphasises the advantage of not having a system that cools down the leaving air stream AL-2 going to a power generating gas turbine.

Table 4: MCM burner, air preheat temperature 850°C

Stream no	A-0	A-1	A-2	AL-1	AL-2	GS-1	EG-1	S-1	EGS-1	OX-1
Mole Frac										
CH4	0	0	0	0	0	0.17419	0	0	0	0
C2+	0	0	0	0	0	0.02657	0	0	0	0
CO2	0.00033	0.00033	0.00033	0.00034	0.00034	0.00635	0.16917	0	0.35985	0
N2	0.77738	0.77738	0.77738	0.80036	0.80036	0.00226	0.00154	0.00000	0.00322	0
O2	0.20854	0.20854	0.20854	0.18514	0.18514	0	0	0	0.00004	1
A	0.00933	0.00933	0.00933	0.00961	0.00961	0	0	0	0	0
H2O	0.00442	0.00442	0.00442	0.00455	0.00455	0.79062	0.82842	1	0.88777	0
Total Flow kmol/se	2.732	2.732	2.732	2.654	2.654	0.166	5.580	0.13159	0.380	0.079
Total Flow kg/sec	79.00	79.00	79.00	76.49	76.49	3.07	0.25	2.37	7.95	2.51
Temperature C	15.0	453.0	850.0	1162.0	763.0	201.0	1170.0	214.0	550.0	1162.0
Pressure bar	1.0	20.0	20.0	20.0	20.0	20.1	19.8	21.0	19.8	20.0
Enthalpy kW	-4091.8	31940.8	67378	93026	57589	-34147	-54519	-31099	-90887	2984

Thus shown in the tables; only the combined process according to the present invention is able to heat the incoming air stream without decreasing the temperature of the leaving air stream from the burner stage (i.e. without heat exchange hot outgoing air stream AL-2 with "cold" incoming air stream A-1).

Thus the process, shown by example, includes a method for preheating air fed to a burner membrane without generating CO_2 in the air stream and without lowering the temperature of the same air stream leaving the membrane burner as shown in Tables 2-4.

Furthermore, as shown in Tables 2 and 3, the exhaust gas stream, EG-4, leaving the burner contains mainly CO_2 and H_2O (steam). After separation of the condensed water the CO_2 gas stream is suitable for direct use in different processes.

The present invention relates to a process where air is:

i) preheated with heat generated from the combustion of a carbon rich fuel with an oxygen enriched sweep gas,

ii) preheated to a temperature level high enough to give significant oxygen fluxes through the membrane in the sweep stage and in the burner stage. The process according to the present invention makes it possible to individually adjusting the temperature level of air and sweep gas fed to the sweep stage and

iii) further heated in the membrane burner to higher temperature levels for increasing the efficiency of power generating turbines.

Thus, the temperature can be risen in such a way that the air is at its maximum level when it leaves the membrane.

The circulating sweep gas transports oxygen from the sweep membrane stage to the heat exchange/combustion stage(s). After combustion the sweep gas will be nearly oxygen free, and thus can again return to the sweep stage to collect and transport oxygen to the combustion/heat exchange stage. Thus, this closed sweep gas loop is an essential part of the present invention. To prevent accumulation of mass, a bleed has to be taken out to balance added fuel and oxygen, preferably after combustion where the sweep gas is nearly free for fuel and oxygen. The sweep gas bleed is mixed with fuel and added to the burner stage.

If the process only comprises a burner membrane stage, all heat (of combustion) has to be generated inside the burner membrane package. Thus, the incoming air (before entering membrane package) has to be heated by heat exchange with the hot outgoing air stream as shown in Fig. 3 (or exhaust gas). Thus the temperature of the leaving air stream is decreased, resulting in e.g. a loss of efficiency in a power generating system (turbine).

In the present invention heat exchange of incoming air with outgoing air can be avoided. The present invention relates to a method for directly utilising a part of the total heat of the combustion for heating air prior to entering the membrane package(s) (in heat exchange stage), simultaneously as another part of total heat of combustion generates heat inside the burner stage. Thus the present invention also involves methods for further heating of gases leaving the sweep membrane stage. The present invention also relates to a method of adding heat to endothermic reactions, e.g. steam reforming for production of syngas ($CO + H_2$). The generation of syngas is favourable at pressures and temperatures typical for the process according to the present invention.

As mentioned, one part of total heat of combustion is used for preheating air and the other part for further heating air leaving the burner stage. Thus heat is generated and directly exchanged to air, according to Fig. 1, in stage A and stage C. Thus, this flexibility of dividing and direct heat generation at places where needed is a characteristic of the present invention.

Another part of the present invention is combining the sweep- and the burner concepts. Compared to running either the sweep concept or the burner concept independently both concepts take advantage of such a combination, especially the burner concept.

The sweep membrane stage shall always be before the burner stage (in direction of incoming air) due to the fact that the sweep concept is more dependent upon higher partial pressure of oxygen on the retentate side than the burner concept with respect to limitations in oxygen flux. This is a crucial feature of the present invention. Thus, by adding a burner membrane unit (stage C) after the sweep stage B, one can take advantage of the high temperature of the oxygen depleted air leaving the sweep stage, and further generate more oxygen (reacting with fuel) on the permeate side of the burner membrane. Thus the combination of the two concepts comprises both preheating air (to the sweep membrane stage) and further heating, the now oxygen depleted air (in a second burner membrane stage). Thus such a combination could prolong the extraction (high fluxes) of oxygen from air in a second membrane unit (burner) which is not possible with only a sweep membrane unit of the same order of size (i.e. membrane area). This last statement is explained with the increasement of oxygen partial pressure on the permeate side of the MCM-sweep membrane compared to the permeate side of the MCM-burner membrane due to the oxygen consumption.

Claims

1. An energy efficient process for generation of heat and power, where a carbon containing fuel is combusted with an oxidant in a MCM-burner for generation of heat, an oxygen depleted air stream and an exhaust gas with a high concentration of CO_2 and a low concentration of NOx,
c h a r a c t e r i s e d i n that
the oxidant is obtained by the following steps:
   a) a compressed air stream is preheated in a first stage (A) to a temperature level above 600 °C,
   b) the compressed and preheated air stream from stage (A) is fed to a second stage (B), including a mixed conducting membrane which is able to separate oxygen from the hot air stream fed to the retentate side of said membrane, where a hot sweep gas picks up the oxygen from the permeate side of said membrane and transports the oxygen to the first stage (A) where a carbon containing fuel is combusted with the oxygen enriched sweep gas for generation of heat utilised for indirectly preheating the air stream in stage (A) by means of a heat exchanger,
   c) passing the oxygen depleted air stream from said second stage (B) into a third stage (C) including the MCM-burner, where the depleted air stream flows on the retentate side of the MCM-burner membrane giving off oxygen to the combustion zone on the permeate side of the membrane, where oxygen (i.e. the oxidant) reacts directly with added fuel on the membrane or close to the membrane surface for generation of heat and a hot exhaust gas stream with a high concentration of CO_2 and low concentration of NO_x.

2. An energy efficient process for generation of heat and power according to claim 1,
   c h a r a c t e r i s e d i n that
   the generated heat in stage (C) is indirectly heating the oxygen depleted air stream in stage (C).

3. An energy efficient process for generation of heat and power according to claim 1,
   c h a r a c t e r i s e d i n t h a t
   the sweep gas is the hot combustion product (the exhaust gas) from stage (A).

4. An energy efficient process for generation of heat and power according to claim 1,
   c h a r a c t e r i s e d i n t h a t
   a bleed stream is taken out from stage (A) and fed to the permeate side of stage (C).

5. Use of the generated heated air stream from the process according to claims 1-4,
   in a power generating plant.

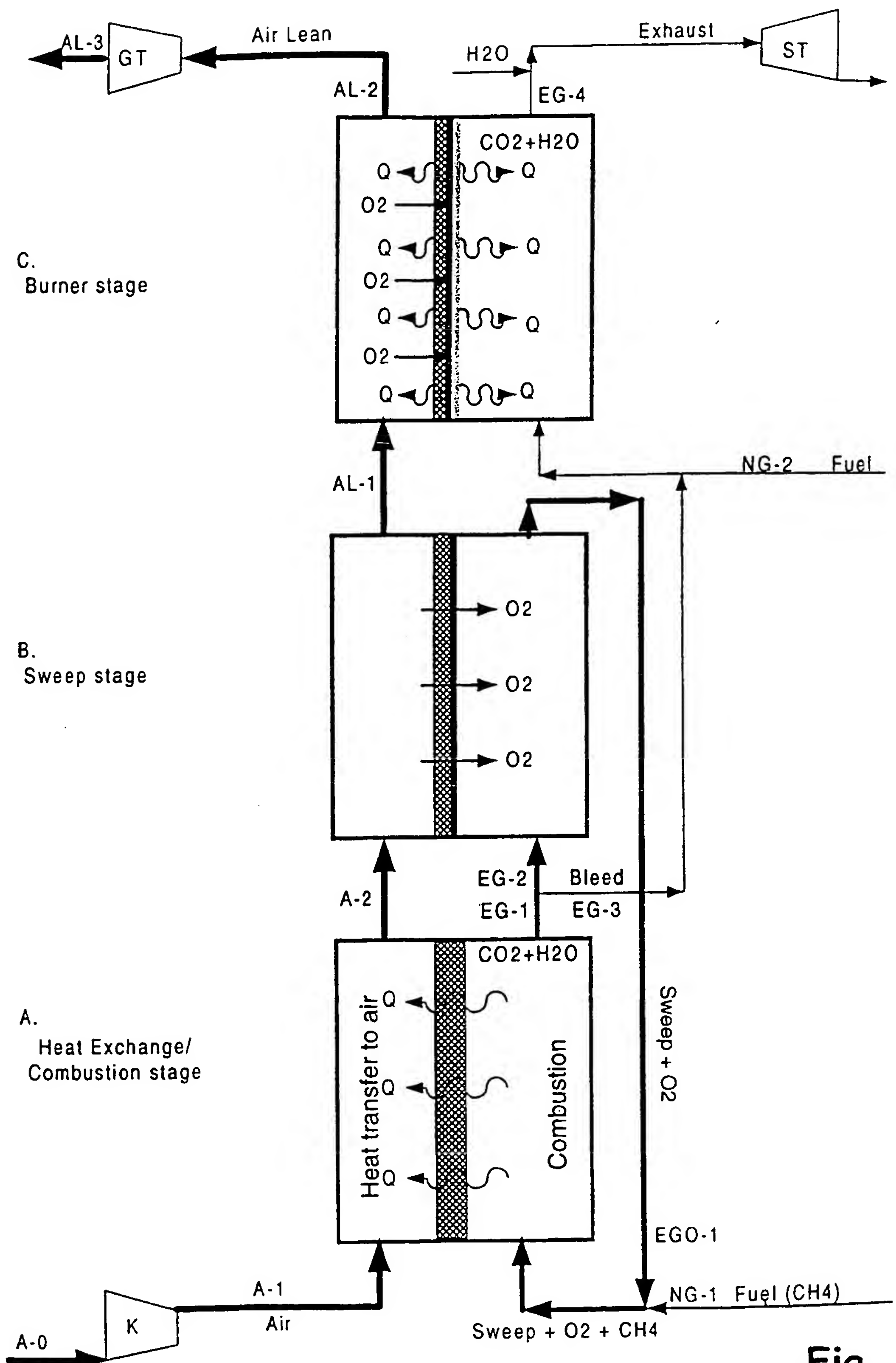
6. Use of the generated heated air stream from the process according to claims 1-4,
   to generate power by depressurizing the oxygen depleted air stream in a turbine and further recovering the heat from the stream leaving the turbine by steam generation and further use of the steam in another power generating turbine.

7. Use of generated heat from the process according to claims 1-4,
   in endothermic reactions.

8. Use of generated heat or exhaust gas from the process according to claims 1-4,
in syngas production.

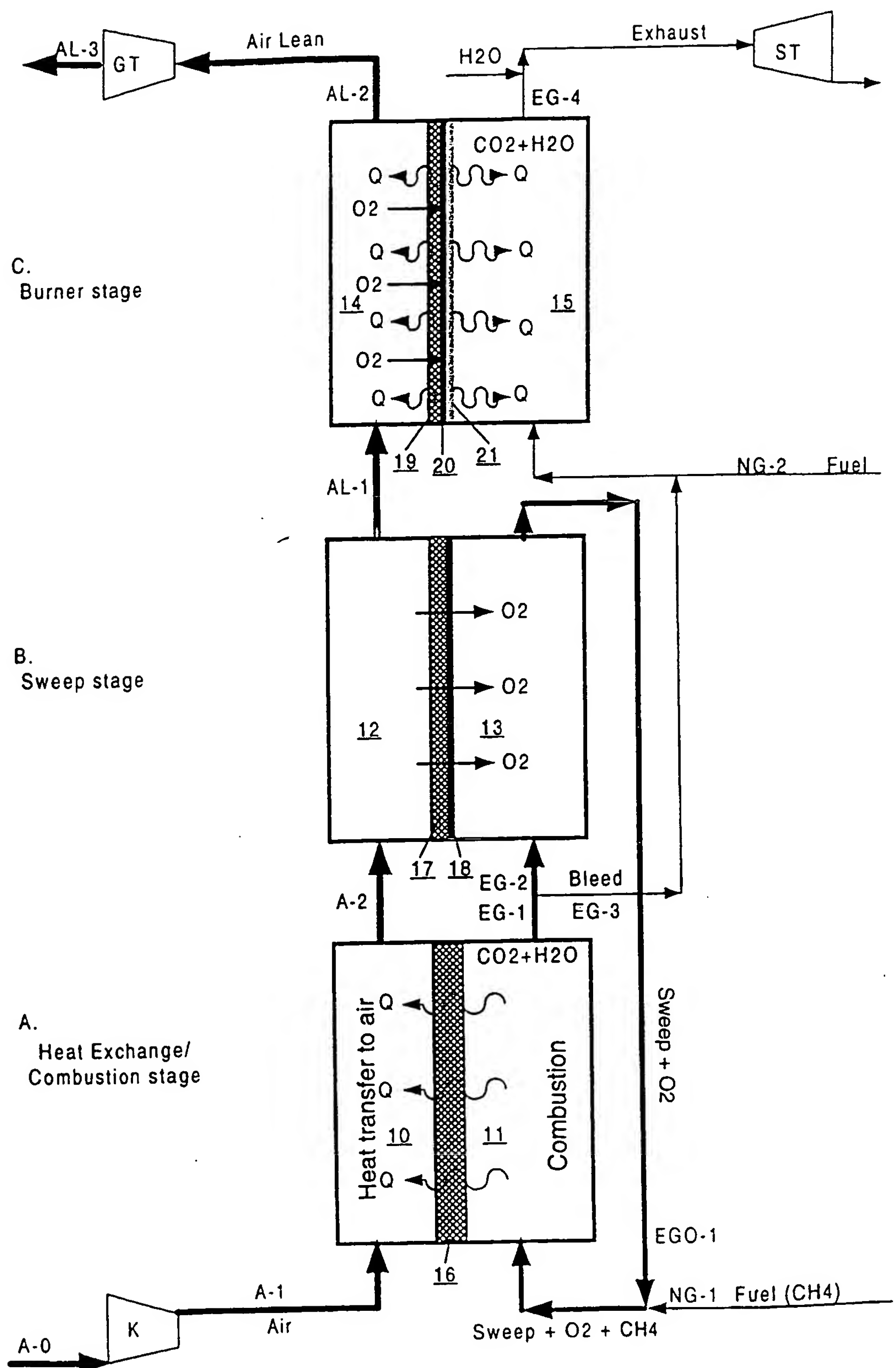
9. Use of generated exhaust gas, from the process according to claims 1-4, in a power generating plant, in different chemical processes or, after removal of water, for injection in a geological formation for long term deposition or for enhanced recovery of oil from an oil reservoir and other forms of deposition.

10. Use of generated exhaust gas from the process according to claims 1-4, to generate power by depressurizing the hot exhaust gas in a turbine and further recovering the heat from the stream leaving the turbine by steam generation and further use of the steam in another power generating turbine.



AL-3
GT
Air Lean
AL-2
H2O
Exhaust
ST
EG-4
CO2+H2O
Q
O2
C.
Burner stage
AL-1
NG-2 Fuel
B.
Sweep stage
A-2
EG-2
EG-1
Bleed
EG-3
CO2+H2O
A.
Heat Exchange/
Combustion stage
Heat transfer to air
Combustion
Sweep + O2
EGO-1
A-0
K
A-1
Air
Sweep + O2 + CH4
NG-1 Fuel (CH4)

Fig. 1



AL-3
GT
Air Lean
AL-2
H2O
Exhaust
ST
EG-4
CO2+H2O
Q
O2
C.
Burner stage
14
15
19
20
21
AL-1
NG-2 Fuel
O2
B.
Sweep stage
12
13
17
18
EG-2
Bleed
A-2
EG-1
EG-3
CO2+H2O
A.
Heat Exchange/
Combustion stage
Heat transfer to air
10
11
Combustion
Sweep + O2
EGO-1
16
A-1
NG-1 Fuel (CH4)
A-0
K
Air
Sweep + O2 + CH4

Fig. 2

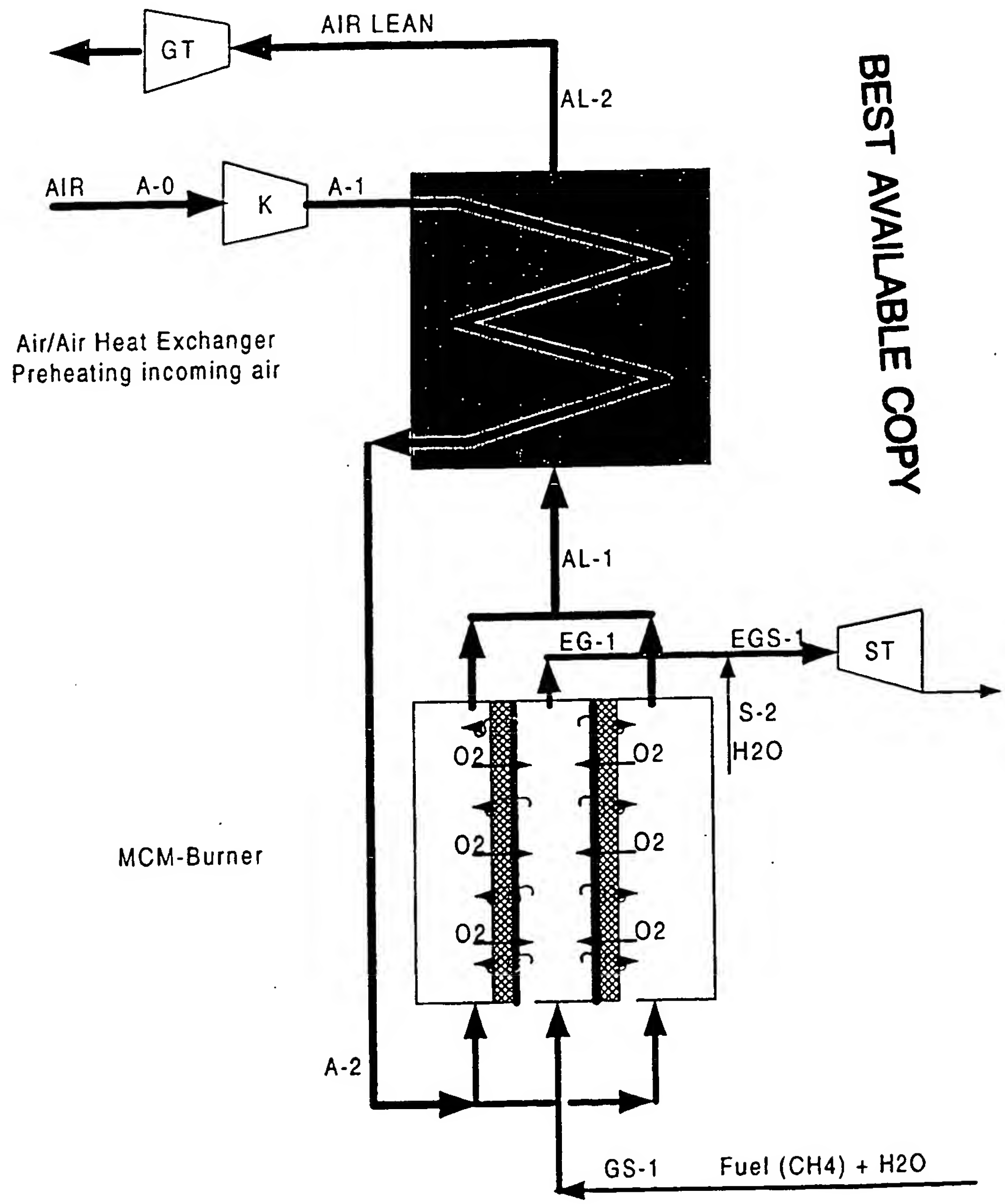

AIR LEAN
GT
AL-2
AIR
A-0
K
A-1
Air/Air Heat Exchanger
Preheating incoming air
AL-1
EG-1
EGS-1
ST
S-2
H2O
O2
O2
O2
O2
O2
O2
MCM-Burner
A-2
GS-1
Fuel (CH4) + H2O

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 01/00163

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: F23C 11/00, B01D 53/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B01D, F23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO INTERNAL, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9855394 A1 (NORSK HYDRO ASA), 10 December 1998 (10.12.98), figure 1, abstract --	1-10
A	US 5562754 A (DOOHEE KANG ET AL), 8 October 1996 (08.10.96), figures 1,2, abstract --	1-10
A	EP 0882486 A1 (PRAXAIR TECHNOLOGY, INC.), 9 December 1998 (09.12.98), page 3, line 40 - page 4, line 10, figure 1, claim 1, abstract -- --------	1-10

☐ Further documents are listed in the continuation of Box C.　☒ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 August 2001	17 -08- 2001
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Bertil Dahl/MP Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

02/07/01

International application No.
PCT/NO 01/00163

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 1015383 A	05/07/00
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		US 5888272 A	30/03/99
		US 6149714 A	21/11/00
		ZA 9804852 A	04/01/99